



The lignin pyrolysis composition and pyrolysis products of palm kernel shell, wheat straw, and pine sawdust



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ABSTRACT

The lignin monomer composition of palm kernel shell (PKS) was characterized using pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), and the characteristics and distributions of products obtained from PKS pyrolysis were investigated using Py-GC/MS, GC, and a specially designed pyrolysis apparatus. The gasification reactivity of PKS biochar was also characterized using thermogravimetry (TG) and Raman spectroscopy. All the results were compared with those obtained from wheat straw (WS) and pine sawdust (PS). The results showed that PKS lignin is primarily composed of *p*-hydroxyphenyl structural units, while WS and PS lignins are mainly made up of guaiacyl units. Both the mass and energy yields of non-condensable gases from PKS pyrolysis were lower than those obtained from WS and PS pyrolysis at 650–850 °C, owing to the lower volatile content (75.21%) and lack of methoxy groups in PKS. Compared with WS and PS, higher bio-oil productivity was observed during PKS pyrolysis. Phenols were the main component of PKS bio-oil from pyrolysis at 500 °C, and the phenol content of PKS bio-oil (13.49%) was higher than in WS bio-oil (1.62%) and PS bio-oil (0.55%). A higher yield of biochar (on an ash-free basis) was also obtained from PKS pyrolysis. Because of its greater relative degree of ordered carbon, PKS biochar exhibited lower in situ reactivity during CO₂ or H₂O gasification than WS and PS biochars. A longer residence time and addition of steam were found to be beneficial during PKS biochar gasification.

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1. Introduction

Oil palm is an important crop, because edible oil can be extracted from oil palm fruit, and so it is commonly planted in tropical areas of the world. Palm kernel shell (PKS) is a solid residue generated as a byproduct of palm oil production. Worldwide, approximately 17.8 million tonnes of PKS was produced in 2011 [1], and this number is gradually increasing as the demand for palm oil continually grows. PKS has been considered as a good quality biomass energy source owing to its great higher heating value (HHV) of 21–23 MJ/kg [2–4]. Currently, PKS is primarily used in low-efficiency direct-fired boiler systems to generate steam in palm oil processing plants. If PKS can be utilized more effectively, the cost of palm oil production could be lowered. In this regard, gasification technology represents a viable means of converting PKS to gaseous fuels, from which electricity and steam can be produced [5].

Pyrolysis is an important sub-step of gasification technology. The yields and properties of pyrolysis products, especially the gasification reactivity of the solid biochar, determine the gasification efficiency to a great extent. To date, some studies pertaining to the pyrolysis characteristics of PKS have been carried out. Yang et al. [2] investigated the PKS pyrolysis characteristics and gas product properties using thermogravimetry–Fourier transform infrared (TG-FTIR) spectroscopy. This work identified four stages in the pyrolysis of PKS at slow heating rates: moisture evaporation, hemicellulose decomposition, cellulose decomposition, and lignin decomposition. Besides, PKS pyrolysis was determined to follow a first order reaction model with an activation energy of 62.85 kJ/mol over the temperature range of 220–340 °C. Ma et al. [6] observed an extra shoulder peak at 279 °C in addition to the main mass loss peak at 358 °C during PKS pyrolysis and attributed this shoulder to the high lignin content in the PKS. Based on these data, it is obvious that the process of PKS pyrolysis is different with those of other biomasses, such as pine sawdust (PS) and bamboo [7,8].

The characteristics of PKS bio-oil were also examined in previous studies [3,9–12]. Yang et al. [3] obtained a maximum mass

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yield of bio-oil (57.31%) from PKS pyrolysis at 500 °C, consisting of a mixture of acids, ethers, phenols and other compounds. Abnisa et al. [9] also reported a maximum bio-oil yield of 46.40% at 500 °C when using a fixed bed. They evaluated the mass yields and characteristics (pH, density, viscosity and water content as well as elemental analysis and FTIR data) of bio-oils from co-pyrolysis of PKS and polystyrene [10]. Asadullah et al. [11] obtained their highest bio-oil yield of 57.00% at 550 °C using a fluidized bed, and found that phenol was the majority product among the identified compounds. Kim et al. [12] discussed the effects of reaction temperature on the yields of phenol and phenolic compounds. In general, higher bio-oil yields and greater relative proportions of phenol were obtained from the pyrolysis of PKS compared with most other biomasses, including hardwood and hornbeam shell [13,14].

Much attention has also been focused on the utilization of PKS biochar, which is considered to be a good candidate for the preparation of activated carbon. Abnisa et al. [9] reported the physico-chemical properties of PKS biochar using FT-IR and scanning electron microscopy. Lee et al. [15] studied the characteristics (elemental composition, pH, pore structure and mass yield) of PKS biochar produced at 500 °C and compared the results to those obtained with sugarcane bagasse, cocopeat, paddy straw and umbrella tree. These previous studies have shown that the yield of biochar is related to both the pyrolysis temperature and lignin content [9,15,16].

From the above reports, it is evident that the typical characteristics of its biochar and bio-oil are closely related to the lignin in the PKS, a factor that has rarely been examined in previous studies. It would therefore be helpful to elucidate the monomer composition of PKS lignin to allow for the optimized utilization of this lignin and the PKS itself.

Biochar gasification using agents such as CO₂ or H₂O is another important step in gasification technology. The thermal degradation characteristics of raw materials impact the efficiency and carbon conversion ratio during gasification but these parameters are also determined by the gasification reactivity of the respective biochars. Unfortunately, information concerning the gasification reactivity of PKS biochar is limited.

Based on the above, the key objectives of the present study were to investigate the distributing characteristics of PKS bio-oil and the gasification reactivity of PKS biochar. These investigations can be classified into three aspects. First, the lignin that is the main component of PKS was isolated using an enzymatic/mild acid hydrolysis method and its monomer composition was characterized by pyrolysis with gas chromatography/mass spectrometry (Py-GC/MS) to better understand the characteristics of PKS bio-oil obtained from pyrolysis. Second, the mass and energy yields of pyrolysis products (that is, biochar, bio-oil and gases) at different pyrolysis temperatures were examined using an apparatus of our own design. Last, the gasification reactivity of PKS biochar was studied using thermogravimetric analysis (TGA) and the carbon structure of the biochar was determined. Comparison tests were conducted under the same conditions using wheat straw (WS) and PS. The results of this study should provide a theoretical reference for the industrial application of PKS gasification with higher efficiency.

2. Experimental

2.1. Materials

The PKS used in this study was obtained from Riau, Indonesia, while the WS and PS were collected in a rural area in Henan Province and a furniture plant in Guangdong Province, China,

respectively. The biomass samples were washed to remove clay and subsequently air-dried under natural sunlight for 6 h. These samples were ground so as to pass an 80mesh screen (particle size ≤ 0.178 mm), then dried in an oven at 105 °C for 24 h to remove moisture.

The elemental compositions of samples were determined using an elemental analyzer (Vario EL III, Elementar, Germany). The volatile matter and ash content were measured in accordance with ASTM E872 and E1755, respectively, and the fixed carbon content was assumed to represent the remainder of the sample mass. The mineral composition of the ash was determined using inductively coupled plasma optical emission spectrometry (Optima 8000, Perkinelmer, USA).

2.2. Isolation of EMAL

The isolation of lignin (EMAL) was based on the enzymatic/mild acid hydrolysis method proposed by Lou et al. EMAL was isolated with high purity (~95%) and yield, and it was considered to be more representatively than industrial lignin [17,18]. The extraction of EMAL as reported in the literature to date typically includes two steps: cellulose enzymatic hydrolysis and mild acidolysis [18]. In this process, a dry biomass sample was first milled and extracted with acetone, and the resulting powder was decomposed with cellulase (Pulpzyme TPE, Puridet, Hong Kong). Following this, the solid residue was treated with an acidic 1,4-dioxane/water mixture. After vacuum rotary evaporation and flocculation, the EMAL was ready for analysis.

2.3. Py-GC/MS analysis

A Py-GC/MS system, consisting of a filament pyrolyzer (CDS 5200, Chemical Data Systems, USA) and a GC/MS (7890A-5975C, Agilent Technologies, USA), was used to separate and identify the fast pyrolysis products of the original biomass and EMAL samples. In each trial, a 0.2 mg sample was loaded into the filament pyrolyzer and immediately heated to 500 °C with a residence time of 10 s. High purity helium was used as the carrier gas (1 L/min) to prevent secondary reactions and the fast pyrolytic products were analyzed by the GC/MS. The operational parameters of the GC/MS were as follows: injector temperature, 300 °C; oven temperature, from 40 °C (held for 2 min) to 300 °C (held for 33 min) at a heating rate of 10 °C/min; HP-5 MS capillary column (12 m \times 0.2 mm \times 0.33 μ m); split ratio, 50:1; EI mode with an ion-source electron energy of 70 eV; spectra acquired from m/z 20–450 and peak identification via the NIST mass spectral library, 2008 version.

2.4. Pyrolysis experiments

2.4.1. Apparatus and pyrolysis procedure

A fast pyrolysis apparatus (see Fig. 1) was employed to investigate the pyrolysis behavior of samples. Briefly, this unit comprised an electric heating furnace, a temperature control system, a 1200 mm (L) \times 40 mm (I.D.) quartz tube reactor and a sample container. In each test, about 5 g of the biomass sample was loaded into a container and then placed at the cold side of the quartz tube. Before each test began, nitrogen (200 mL/min) was used as an inert gas to purge air from the interior of the reactor for 30 min. The quartz tube reactor was heated electrically and the temperature in the reactor was monitored using a K-type thermocouple. Once the reactor had stabilized at the target temperature (650, 700, 750, 800 or 850 °C), the container with the biomass sample was moved into the heated zone and held there for 10 min to allow the contents to react completely. The reactor was taken out of the furnace after the pyrolysis reaction and allowed to naturally

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